N-Benzoyl-N-phenylhydroxylamine as a Reagent for the Separation of Niobium-95 from Zirconium-95 and for the Spectrophotometric Determination of Zirconium and Niobium

Tsunenobu SHIGEMATSU*, Yasuharu NISHIKAWA**, Shiro GODA** and Hiroshi HIRAYAMA**

(Shigematsu Laboratory)

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The solvent extraction and the spectrophotometric determination of Zr and Nb were investigated using N-benzoyl-N-phenylhydroxylamine (NBPHA) as a chelating reagent. With 0.1% NBPHA in $CHCl_3$, more than 98% of Zr is extracted from 0.05～0.1N H_2SO_4 solution and 95% or more of Nb is extracted from 12～15N H_2SO_4 solution. Since Zr is completely left in aqueous phase under the optimum extracting condition for Nb, the extraction procedure can be applied to the separation of ^{95}Nb from ^{95}Zr. Zirconium- and Nb-chelates extracted show light absorption in ultraviolet and near ultraviolet region, and therefore the procedure is also adapted for the photometric determination of these metal ions. When absorbances are obtained at 350 mμ or 360 mμ, Beer's law is followed up to 20 p.p.m. of both ions, and the molar extinction coefficients of Zr are 5,200 at 350 mμ and 2,950 at 360 mμ; and those of Nb are 4,250 at 350 mμ and 3,050 at 360 mμ, respectively.

INTRODUCTION

During the past ten years, the several methods of the liquid-liquid extraction have been proposed for the separation of zirconium-95 and niobium-95. Much of these methods were based on the principle that zirconium was transferred into organic solvent phase and niobium was left in aqueous phase. For example, in Scadden and Ballou's research using 0.06M DBP in dibutyl ether as an extracting solvent, at least 99% of zirconium-95 was removed into organic phase from 1M mineral acid solution and about 98% of niobium remained in the aqueous phase[1]. Umezawa and Hara[2] extracted zirconium-95 with 0.005M trioctylphosphine oxide (TOPO) in carbon tetrachloride, leaving niobium-95 in the aqueous 2N nitric acid solution. β-Diketones were recognized to be excellent reagent for the separation of these two nuclides. Zirconium-95 was separated from niobium-95 by extracting with 0.5M TTA in xylene or with 0.5M TTA in benzene from 1～6N hydrochloric acid or from 2N nitric acid solution[3,4,5]. Acetylacetone[6,7], trifluoroacetylacetone and benzoyltrifluoroacetone[8] were also utilized for the extracting separation of zirconium-95 from niobium-95.

However, because niobium-95 is a daughter nuclide of zirconium-95 and

* 重松　恒信
** 西川　泰治，合田　四郎，平山　宏，Kinki University, Fuse.

grows up by the decay of the latter, it is considered to be more favourable way to extract niobium-95 into organic phase and to leave zirconium-95 in aqueous phase for the future milking. As the extraction procedure for niobium, the fluoride system has been commonly recommended[9),10)], and Milner and coworkers[11)] suggested the separation of niobium and zirconium, that is, the distribution coefficient of 2.5×10 for niobium and that of 1×10^{-3} for zirconium were given, when the extraction was carried out with hexone from the solution containing $10M$ hydrofluoric acid, $6M$ sulphuric acid and $2.2M$ ammonium fluoride. Nevertheless, the fluoride system has a serious weakness that glass vessels can not be used.

Recently it was found that N-benzoyl-N-phenylhydroxylamine (NBPHA) might be available for extracting niobium. Since this compound, a derivative of cupferron is more stable than the latter substance and is much better reagent[12)], it has been widely employed as a precipitant for many metal ions[13)]. Dyressen[12)] applied this reagent to the extraction of lanthanum (III), thorium (IV) and uranium (VI) from a weak acidic solution, and separated lanthanum from thorium and uranium at pH 4.5 by using $0.1M$ NBPHA in chloroform. Alimarin and Petrukhin[14)] investigated the extraction behaviour of NBPHA chelates of niobium (V), tantalum (V) and vanadium (V) in detail, and reported that 99.9% of niobium could be extracted from $12\sim24N$ sulphuric acid and zirconium from $1\sim2N$ sulphuric acid solution with $0.1M$ NBPHA in chloroform.

Quite recently a convenient method for the carrier-free separation of niobium-95 from zirconium-95 using this reagent was proposed by Lyle and Shendrikar[15)]. Niobium-95 was separated by extracting with 0.2% NBPHA in chloroform from aqueous $0.05M$ hydrofluoric and $1M$ hydrochloric acid solution, and by stripped into aqua regia, ammoniacal $7M$ hydrogen peroxide, or into $6M$ aqueous ammonia.

Separately from these investigations, the authors have also studied the extraction of zirconium and niobium using NBPHA as a chelating reagent, and found the optimum condition to extract zirconium and niobium and to separate the latter from the former without the use of hydrofluoric acid which required polyethylene vessels. And furthermore it was revealed that zirconium and niobium could be determined spectrophotometrically, because these metal-NBPHA chelates show light absorption in ultraviolet and near ultravolet region. In this paper the extraction behaviour of these two metal ions were described, the separation procedure of niobium-95 from zirconium-95 was recommended, and the spectrphotometric methods for the determination of zirconium and of niobium were established.

APPARATUS AND MATERIALS

The radioactivity countings were made with a Kobe Kogyo NaI(Tl) (3″×3″) well-type scintillation counter, model PS 300, connected to a scaler, model SA 200 and with a Toshiba radiation model EAG-31103B using a AEN endwindow-type GM tube 132A. A Hitachi photoelectric spectrophotometer, model EPU-2A was used for the light absorption measurements.

Zirconium-95 and niobium-95 tracer solution: Zirconium-niobium-95 mixture supplied in a 0.5% oxalic acid solution, from The Radiochemical Center, Amersham, England, was converted to sulphate sulution by fuming with sulphuric acid. Zirconium-95 and niobium-95 tracer solutions were prepared by TTA extraction method: Zirconium-95 was extracted with $0.5M$ TTA benzene solution from $2N$ nitric acid solution containing small amount of hydrogen peroxide, while niobium-95 remained in aqueous layer. Organic and aqueous phases were evaporated, fumed with perchloric acid and the residues were dissolved in water to give about 1 μc./ml. solutions. The radiochemical purities of these tracers were confirmed by estimating the maximum energy of beta rays.

Zirconium standard solution, 100 μg./ml. Zirconium oxide (ZrO_2) was fused with potassium carbonate, and dissolved with appropriate amounts of $2N$ sulphuric acid.

Niobium standard solution, 100 μg./ml. Niobium oxide (Nb_2O_5) was fused with potassium carbonate, and dissolved with dilute potassium carbonate solution.

N-Benzoyl-N-phenylhydroxylamine (NBPHA) solution, 0.1%: 0.1 g. of NBPHA (from Dojindo and Co. Ltd., Research Laboratories) was dissolved in 100 ml. of chloroform.

All other reagents used in this experiment were the reagent grade materials.

EXPERIMENTAL RESULTS AND DISCUSSION

Extraction Behaviour of Zirconium and Niobium

Extracting procedure. The extraction behaviour of zirconium- and niobium-NBPHA chelate was studied by the following procedure:

To a solution containing about 1 μc. of zirconium-95 or of niobium-95 and 10 μg. of the carriers (except in the carrier-free experiments) a proper amount of sulphuric acid is added, and the volume of the solution is adjusted to 10 ml. in a 50 ml. separating funnel. Ten milliliters of 0.1% NBPHA solution in chloroform are mixed with the resulting solution and the mixture is shaken for 2 minutes (for the extraction of zirconium) or for up to 1 hour (for niobium). After the organic and aqueous phases are separated, 2 ml. of counting samples are taken from each of two phases and transfered into polyethylene tubes, and the gamma rays are measured with the NaI(Tl) scintillation counter.

The distribution ratio, D, is obtained from the gamma activities of both phases, and then the per cent extraction, E, is calculated from the distribution ratio by the following equations,

$$D=\frac{\gamma\text{-activity in organic phase}}{\gamma\text{-activity in aqueous phase}}$$

$$E(\%)=\frac{1}{1+D}\times 100$$

Influence of sulphuric acid concentration. Figure 1 and Fig. 2 show the dependence for the extraction of zirconium and of niobium on the acidity of sulphuric acid, respectively. As shown in Fig. 1, at least 98% of zirconium can be extracted from aqueous $0.05\sim0.1N$ sulphuric acid solution, but the extraction

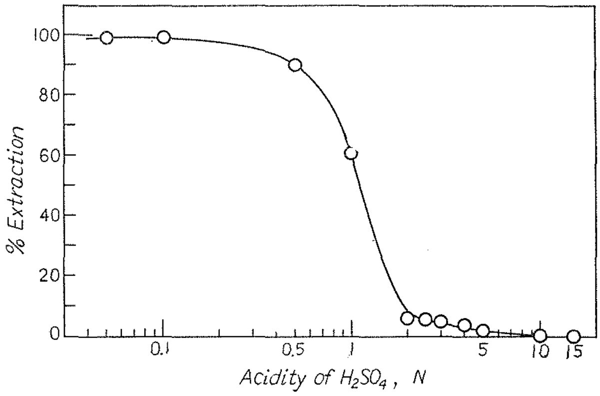

Fig. 1. Effect of sulphuric acid concentration on the extraction of zirconium.

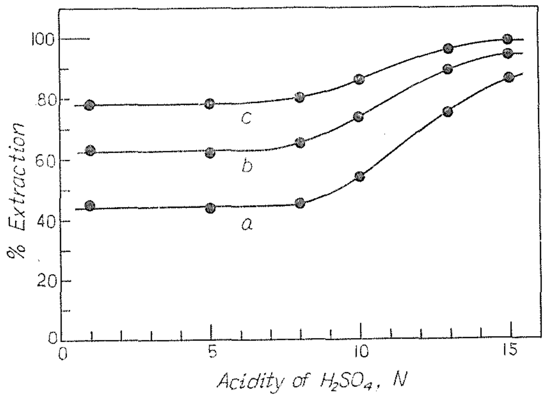

Fig. 2. Effect of sulphuric acid concentration on the extraction of niobium.
Shaking time, a : 10 min, b : 30 min, c : >1h.

yield rapidly decreases with the increase of the acid concentration, and in sulphuric acid medium above $5N$ zirconium almost completely remains in aqueous phase, even when the shaking follows for 1~2 hours.

Quite different from this, the extractability of niobium rises with the increase of the acidity, and more than 95% of niobium is extracted from aqueous 12~$15N$ sulphuric acid solution. In this case, however, it is somewhat time-consuming to reach the equilibrium, and the shaking must be least for 1 hour, as seen from Fig. 2.

Effect of NBPHA concentration. The effect of NBPHA concentration is shown in Fig. 3, which is obtained by extracting zirconium from $0.1N$ sulphuric acid and niobium from $12N$ sulphuric acid solution. The figure indicates that the satisfactory extractions can be achieved by using 0.1% or more of the reagent in chloroform.

Effect of diverse substances. The influence of diverse ions was examined by adding several kinds of substances into aqueous sample solution before the extracting procedure is done*. The results are summerized in Table 1. Among

* Extractions are made with 0.1% NBPHA chloroform from $0.05N$ sulphuric (for zirconium) or from $12N$ sulphuric acid medium (for niobium).

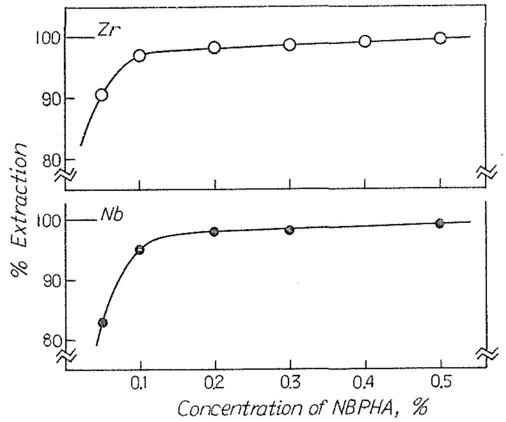

Fig. 3. Effect of NBPHA concentration.
—○— zirconium, —●— niobium.

Table 1. Effect of diverse substances.

Substance added	Extraction %	
	Zr*a)	Nb*b)
0.1*M* Na_2SO_4	98.5	98.6
0.1*M* NaCl	96.9	98.7
0.1*M* NaF	7.5	95.6
0.1*M* CH_3COONH_4	95.9	71.3
0.1*M* $H_2C_2O_4$	4.4	51.0
0.3% H_2O_2	95.6	66.6

* Extractions were made from a) 0.05*N* sulphuric and b) 12*N* sulphuric acid solution.

the substances studied sodium fluoride and oxalic acid interfer the extraction of zirconium, while ammonium acetate, oxalic acid and hydrogen peroxide affect the extraction of niobium.

Separation of Niobium from Zirconium

From the above experimental results it seemed to be possible that the extraction with NBPHA is applied to the separation of niobium-95 from zirconium-95, and therefore the following procedure was proposed.

Ten milliliters of zirconium- niobium-95 mixture solution containing sulphuric acid in the final concentration of 12*N*, is shaken with an equal volume of 0.1% NBPHA chloroform for 1 hour. After two phases are separated, the organic phase is washed with 10 ml. of 12*N* sulphuric acid, evaporated at room temperature, and is fumed with the mixture of sulphuric and perchloric acid, —Niobium-95 fraction. On the other hand, after washing with 10 ml. of 0.1% NBPHA chloroform, the aqueous phase is evaporated and fumed with sulphuric acid,— Zirconium-95 fraction.

Aluminium absorption curves of beta rays for the niobium-95 fraction and the zirconium-95 fraction were measured by using point sources on thin Mylar film, and results are shown in Fig. 4 and Fig. 5, which indicate that the radio-

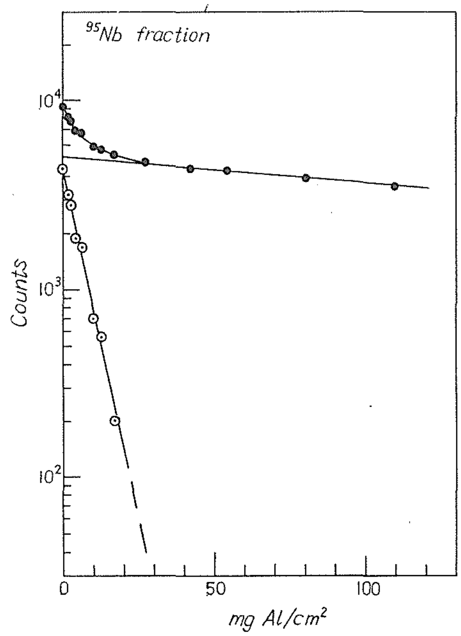

Fig. 4. Aluminium absorption curve of niobium-95 fraction.

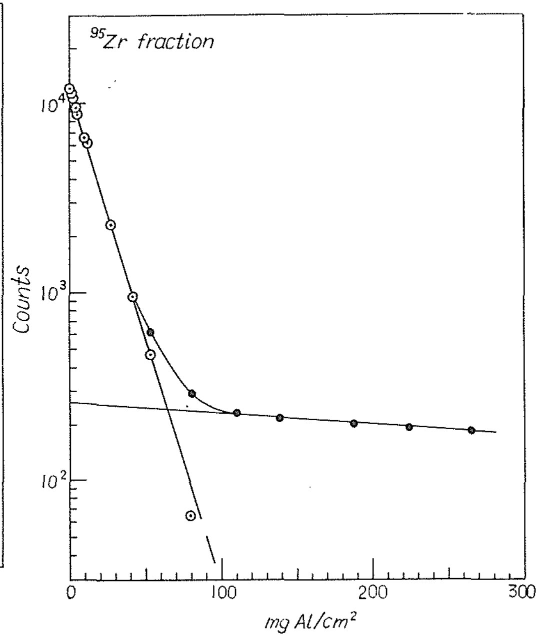

Fig. 5. Aluminium absorption curve of zirconium-95 fraction.

chemically pure niobium-95 and zirconium-95 can be successfully separated by this NBPHA extraction method.

Spectrophotometric Detemination of Zirconium and Niobium

Zirconium- and niobium-NBPHA chelates extracted in chloroform show relatively intense light absorption in ultraviolet and near ultraviolet region, and accordingly was investigated the application of the above described extraction procedure to the spectrophotometric determination of these metal ions*.

The absorption spectra of zirconium and niobium chelates in 0.1% NBPHA chloroform are shown in Fig. 6. Absorbances were obtained against the reagent blank, of which absorption curve is also indicated in the figure. Although zirconium chelate has an absorption maximum near 330 mμ and niobium chelate might show at a some shorter wave length, the accurate measurements at such a wave length are difficult or impossible, because of much intense absorption attributed to the reagent in this region (below 350 mμ). Consequently, it is reasonable that absorbances at 350 mμ or 360 mμ are used for the defermination of zirconium and of niobium, though the sensitivity is of course considerably lowered.

Figure 7 represented the calibration curves for the determination of zirconium and niobium; Beer's law is obeyed in the range from 1 p.p.m. to 20 p.p.m., and the molar extinction coefficients are 5,200 at 350 mμ, 3,950 at 360 mμ for zirconium,

* Possibility for the determination of niobium is already suggested in Stary's publication. (J. Stary, "Extraction of Metal Chelates", Pergamon press, (1964), p. 124)

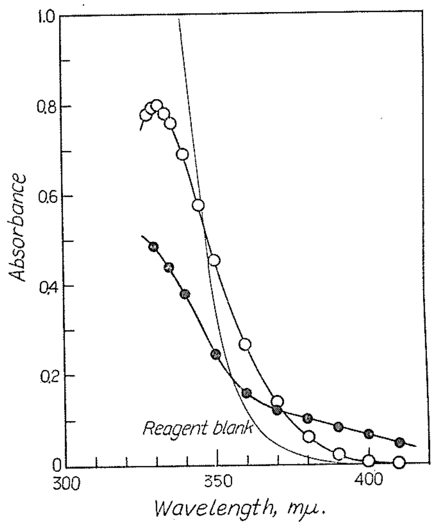

Fig. 6. Light absorption spectra of zirconium and niobium chelate.
—○— zirconium chelate, —●— niobium chelate.

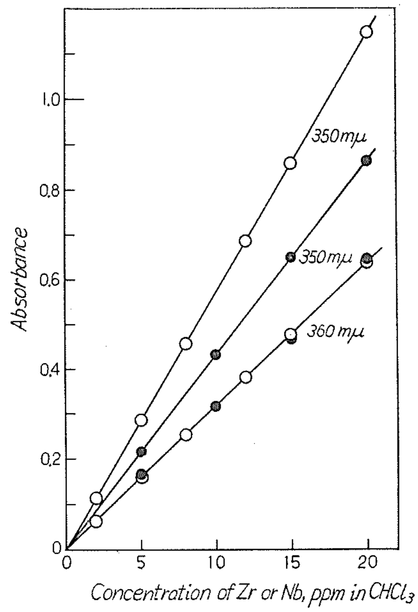

Fig. 7. Analytical curves for zirconium and niobium.
—○— zirconium, —●— niobium.

and 4,250 at 350 mμ, 3,050 at 360 mμ for niobium.

Analytical procedure: The following procedures were designed for the determination of zirconium and of niobium.

Zirconium: Sample solution containing 10~200 μg. of zirconium is taken in a 50 ml. separating funnel. After added 5 ml. of 1*N* sulphuric acid and diluted to 10 ml, the solution is shaken with 10 ml. of 0.1% NBPHA chloroform solution for about 2 minutes. Chloroform phase separated is dehydrated with anhydrous sodium sulphate, and after standing for about 10 minutes*, the absorbances are obtained against the reagent blank at 350 or 360 mμ.

Niobium: Sample solution containing 10~200 μg. of niobium is treated in the same way as in the case of zirconium, except that 8 ml. of 15*N* sulphuric acid is added instead of 5 ml. of 1*N* sulphuric acid. And absorbances must be obtained between 30 and 90 minutes after the end of the extraction.

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* Absorption attains the full value at 10 minutes after the extraction and keeps at constant value at least for 1 hour.

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